PBL Netherlands Environmental Assessment Agency

DECARBONISATION OPTIONS FOR THE DUTCH CARBON BLACK INDUSTRY

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Decarbonisation options for the Dutch carbon black industry

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MIDDEN project coordination and responsibility
The MIDDEN project (Manufacturing Industry Decarbonisation Data Exchange Network) was initiated and is also coordinated and funded by PBL and ECN part of TNO (which is named TNO EnergieTransitie since 1-1-2020). The project aims to support industry, policymakers, analysts, and the energy sector in their common efforts to achieve deep decarbonisation. Correspondence regarding the project may be addressed to:
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This report has not been reviewed by Cabot B.V. PBL and TNO remain responsible for the content. The decarbonisation options and parameters are explicitly not verified by the companies.

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Summary

Carbon black is a product widely used in industry to enhance the mechanical, electrical and optical properties of the materials where it is integrated as a filler. Most of the industrially produced carbon black is consumed by the tyre manufacturing industry and the remainder is used in rubber products and diverse applications such as plastics, paint and printing ink.

In the Netherlands the only carbon black manufacturer is Cabot B.V., which has a production capacity of 80,000 tonnes carbon black/year. This plant manufactures different grades of carbon black through the use of furnace black reactors, the predominant method for carbon black production. Cabot B.V. is situated in the Botlek area in the Port of Rotterdam. From 2008 to 2018, the Botlek plant's greenhouse gas emissions ranged from 195 to 247 kilotonnes CO_2-eq.

Carbon black is produced in a reactor using liquid hydrocarbons (feedstock), natural gas (fuel) and air (oxidant). The resulting product is a mixture of tail gas and suspended carbon black. Through filtration, the tail gas and fluffy carbon black are separated and made available for further processing. Direct greenhouse gas emissions result from the combustion of the tail gas in the plant. The energy consumption and the emission factor are approximately 44 GJ/tonne carbon black and 3.3 tonne CO_2/tonne of carbon black, respectively.

Table S1 Energy flows per tonne of carbon black produced

(GJ/tonne carbon black)		
Energy consumption	Electrical	1.8
	Thermal[1]	42.1
	-of which natural gas	8.3
	-of which oil	33.8
	Total	**43.9**
Tail gas use	Dryers	5.7
	Boilers	13.3
	Total	**19.0**
Steam production	Sold to Linde Gas & Kemira	6.4
	Steam turbine	4.2
	Total	**10.6**
Electricity output	Steam turbine	1.8
	Total	**1.8**

The main decarbonisation options for the industrial production of carbon black that have been identified are:

- Electrification of the process through plasma technology, which has already been developed and scaled up. These technologies also produce hydrogen. The carbon black manufactured in the plasma reactor is further processed in order to deliver the final product (pelletized carbon black). For the drying process, steam from an electric boiler can be used.

[1] The thermal energy refers to the energy harvested from the incomplete oil combustion and the complete natural gas combustion within the reactor.

- Carbon capture is a mature technology that could be used to capture CO_2 from the flue gas. In the future, services for CO_2 transport and storage could be contracted in the Port of Rotterdam. The captured CO_2 can also be delivered to greenhouses or used in nearby industries.
- Bio-SNG (Substitute Natural Gas) obtained from biomass can substitute natural gas use in the reactor. Bio-SNG can be produced by upgrading biogas or synthetic gas to the same quality as natural gas. Possibly, biogas that has not been upgraded may be used as well. This may affect the quality of the product or the conditions in the reactor.

Furthermore, the hydrocarbon feedstock (oil) could be substituted by bio-based feedstocks e.g. pyrolysis oil and/or bio-SNG. However, the former is at an experimental state and the latter has limited yields. Finally, carbon black could also be recycled from tyre waste through a pyrolysis process. The company Black Bear transforms used tyres into carbon black in a plant located in Nederweert.

FULL RESULTS

Introduction

This report describes the current situation for carbon black production in the Netherlands and the options and preconditions for its decarbonisation. The study is part of the MIDDEN project (Manufacturing Industry Decarbonisation Data Exchange Network). MIDDEN aims to support industry, policy makers, analysts and the energy sector in their common efforts to achieve deep decarbonisation. Mapping decarbonisation options is an ongoing process. The MIDDEN project will update and elaborate further on options in the future, in close connection with the industry.

Scope

Carbon black is a product widely used in the industry to enhance the mechanical, electrical and optical properties of materials in which it is integrated as a filler. Most of the industrially produced carbon black is consumed by the tyre manufacturing industry and the remainder is used in rubber products and diverse applications such as plastics, paint and printing ink.

The Cabot B.V. plant is situated in the Botlek area in the Port of Rotterdam and is the only manufacturer of carbon black in the Netherlands.

- Production location: Cabot B.V..
- Process: Furnace black process.
- Product: Carbon black.

The main decarbonisation options are the electrification of the process (using plasma technology and electric boilers), Carbon Capture, Utilisation and Storage (CCUS), and substitution of the current fuel (natural gas) by bio-SNG or biogas.

Reading guide

Section 1 introduces the Dutch carbon black industry. Section 2 describes the current situation for carbon black production processes in the Netherlands, and Section 3 describes the products that are produced in these processes. Options for decarbonisation are examined in Section 4. The feasibility of these decarbonisation options is discussed in Section 5.

1 Carbon black production in the Netherlands

This section presents an overview of carbon black production in the Netherlands. First the history is introduced briefly. Afterwards, the Cabot B.V. plant in Rotterdam is described, including its main characteristics, corporate group and greenhouse gas emissions.

Carbon black production in the Netherlands
The carbon black industry is highly dependent on the automotive industry, as it is the largest consumer of carbon black. In 1882, when the automotive industry was emerging, Cabot Corporation decided to buy and establish its first carbon black plant in the USA. Later, the corporation started to operate in Europe, settling first in the UK in 1948. In 1959, expansion to the Netherlands resulted in the construction of a soot factory in the Botlek area of the Port of Rotterdam together with the Dutch chemical company Ketjen. At this time the plant was called Ketjen Carbon and operated as a producer of soot for the car tyre industry. Cabot assumed control of this plant in 1981 under the name of Cabot B.V.. Cabot B.V. exclusively manufactures black carbon since 1995 (Cabot Corporation, 2018).

In the Netherlands there used to be two plants that produced carbon black. Both were located in the Botlek area. In 2010, each plant had a production capacity of 80 kilotonnes/year (Port of Rotterdam, 2010). However, Evonik Carbon Black closed and currently Cabot B.V. is the only producer operating with a production capacity of 80 kilotonnes/year (Port of Rotterdam, 2016).

The Cabot B.V. plant
The Cabot B.V. plant is located in the Botlek area of the Port of Rotterdam (see Figure 1)[2]. The Port of Rotterdam is an important industrial area which includes 122 industrial sites that provide products and services (Port of Rotterdam, Facts and Figures, 2016). The industries can be classified in four main groups:

- Oil and oil products (oil refining, tank and refinery terminals).
- Chemicals, biofuels and edible oils.
- Gas and power, coal and biomass.
- Pipelines and utilities.

[2] Address: Cabot B.V., Botlekstraat 2, 3197 KA, Botlek Rotterdam.

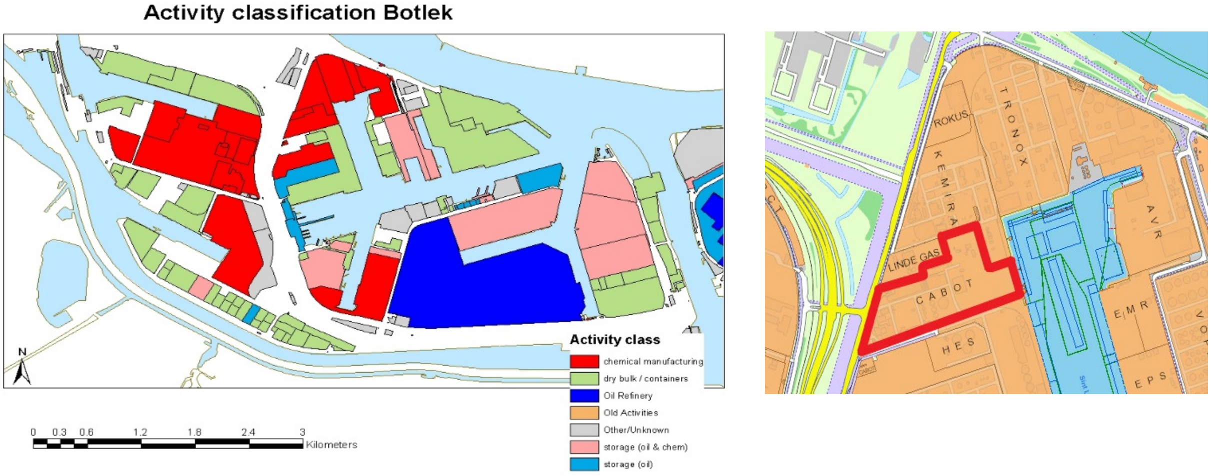


Figure 1 Left: Map of the Botlek area (Deltares, 2013). Right: Location of the Cabot B.V. plant (Port of Rotterdam, 2018)

The Cabot B.V. plant is identified as a chemical manufacturer and has four production units (DCMR, Permit BES98395719, 2012), manufacturing different grades of carbon black in a closed system[3]. The plant uses the furnace black process, which is the most widely used method for carbon black production (European Commission, 2007). Cabot B.V. has 105 employees at the site (Facts and Figures, 2016). The plant operates continuously (DCMR Milieudienst Rijnmond, 2012), producing carbon black that is used as a pigment, reinforcement filler and UV protector in rubber products, plastics, printing industries and coatings.

Cabot Corporation is a global specialty chemicals and performance materials company, headquartered in Boston, with approximately 4,500 employees worldwide (Cabot Corporation, 2020). Cabot Corporation has four business segments (see Figure 2). The largest are the ‘Performance Chemicals’ and ‘Reinforcement Materials’ segments, which together accounted for 88% of total revenues in 2017 (Cabot, Annual Report, 2017). The Botlek plant is specialized in these two segments. Cabot Corporation also owns the Cabot Norit Nederland B.V. plant in Klazienaveen, which produces activated carbon. The plant in Klazienaveen is not covered in this report, but in the MIDDEN-report ‘Decarbonisation options for the Dutch activated carbon industry’ by the same authors.

In 2017, the Cabot Corporation realised a net income of 241 million USD. 80% of the revenues came from outside the U.S. The main sectors that use Cabot products are transportation (60% of the revenues) and the industrial sector (25% of revenues). The sales can be affected by the cyclical nature of the automotive industry (Cabot, Annual Report, 2017).

[3] The closed system enables the transportation of the carbon black from the start to the end of the process through a system of pipelines.

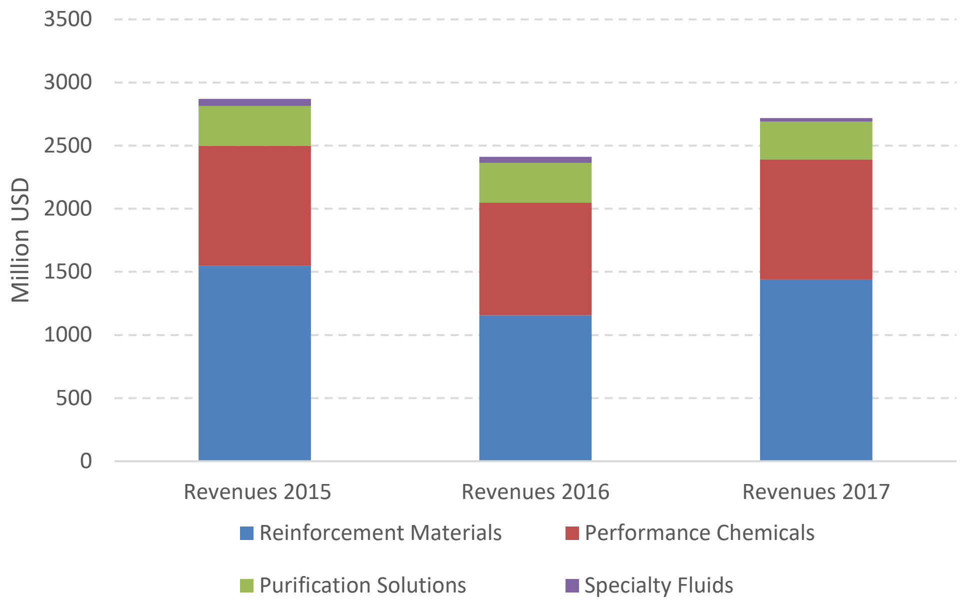


Figure 2 Cabot Corporation revenues by business segment (Cabot, Annual Report, 2017)

Cabot B.V. participates in the European Union Emission Trading Scheme (ETS). From 2008 to 2018, the Botlek plant's greenhouse gas emissions ranged from 195 to 247 kilotonnes CO_2-eq reaching a maximum level in 2016 (NEa, 2018). The increase in emissions from 2015 to 2016 has been attributed to an increase in the production volume from 66,538 to 74,508 tonnes (Deloitte, 2016). Figure 3 provides the trend of the emissions from 2008 to 2017. Data from the Pollutant Release and Transfer Register (Emissieregistratie, 2020) on the emissions of Cabot B.V. show that the contribution of CH_4 to the total greenhouse gas emissions is minor (see Table 1). According to the EU Joint Research Centre (JRC), the total greenhouse gas emissions due to the production of carbon black in Europe were 1.8 megatonne CO_2-eq in 2013 (Boultamani & Moya Rivera, 2017).

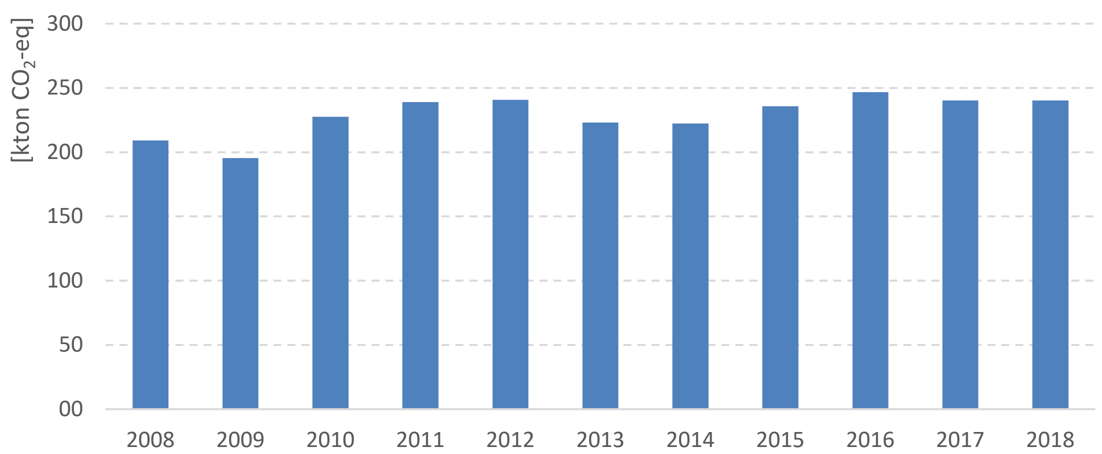


Figure 3 Greenhouse gas emissions per year of the Cabot B.V. plant (permit number: NL-200400203). Source: (NEa, 2018).

Table 1 Greenhouse gas emissions from the Cabot B.V. plant in 2017.

Greenhouse gas	Emissions[4] (tonnes/year)	GWP[5] (Global Warming Potential)	Emissions (kilotonne s(CO_2-eq)/year)
CO_2	240,200	1	240
CH_4	2.7	25	0.07

4 Values provided by the Pollutant Release and Transfer Register (Emissieregistratie, 2020).
5 Values provided in the IPPC Fourth Assessment Report (Parry, Canziani, Palutikof, van der Linden, & Hanson, 2007)*)*.

2 Carbon black processes

This section describes the furnace black production process. First, an overview of the process is presented. Next, the mass balance, energy balance and emissions for the production process in the Cabot B.V. plant are estimated.

2.1 Carbon black production at Cabot B.V.

The Cabot B.V. plant produces carbon black through the furnace black process. This is a process which relies on incomplete feed combustion and represents the predominant method for carbon black production. Globally, approximately 95% of the carbon black was produced in a furnace black reactor in 2002 (European Commission, 2007). The reason behind its extensive use is that it can produce all carbon black grades required by the rubber industry.

The production process
The Cabot B.V. plant manufactures different grades of carbon black simultaneously. There are four production units with a total of six reactors (units 1, 3 and 4 have one reactor each, while unit 2 integrates three small reactors). The Botlek plant has been reported to produce ca. 23 kilotonnes of dry granulate and 52 kilotonnes of wet granulate per year, with a total production volume of 75 kilotonnes/year in 2012. The annual production depends on the customer demand (DCMR Milieudienst Rijnmond, 2012). In 2016, the capacity was 80 kilotonnes/year (Port of Rotterdam, Facts and Figures, 2016).

Carbon black is produced in a reactor where liquid hydrocarbons (feedstock), natural gas (fuel) and air are introduced. The process can be divided into five sections which are interconnected through a closed system containing gases and carbon black in the form of powder:

1) Storage facilities for feedstocks;
2) Reactor;
3) Separation of carbon black and tail gas;
4) Final processing of carbon black, and
5) Tail-gas use.

The feedstocks are conveyed into the core unit of the process: the reactor. The resulting product is a mixture of tail gas and suspended carbon black. This mixture is first cooled and conducted to the collecting system where the solids are separated from the tail gas. Subsequently, the fluffy carbon black is densified into powder black or pelletized. Finally, the pelletized carbon is transported to the storage and packaging area.

The primary and secondary feedstock
Two inputs are fed into the reactor. On the one hand there is the so-called primary feedstock, commonly carbochemical or petrochemical oils. On the other hand there is the so-called secondary feedstock (also called fuel as it is completely combusted in the reactor). The secondary feedstock is commonly natural gas.

The primary feedstock is volatilised leading to the formation of carbon black as particles and aggregates. Commonly used primary feedstocks are carbochemical (coal tar) oils and petrochemical oils as a consequence of their high aromatic hydrocarbon content. The presence of aromatics in the feedstock with a high ring number (e.g. anthracene) are of particular interest as they are known to lead to an increase in carbon black product yield.

Petrochemical oils are the most common feedstock used in the furnace black process. These oils are steam cracker oils, catalytic cracker oils or aromatic concentrates. In Europe, steam cracker oils are more commonly used due to their larger availability. Moreover, their content in sulfur is low (Donnet, 1993). In the past natural gas was the main primary feedstock, however due to economic factors carbochemical and petrochemical oils have been increasingly adopted. The composition of the primary feedstocks is complex and the components influence the quality of the product. Therefore, the selection of the primary feedstock strongly influences overall efficiency, price and product properties/quality.

The primary feedstock is stored in heated tanks at 70 – 120 °C (Donnet, 1993) to avoid crystallization. The feedstock must be heated to 150 – 250 °C before entering the reactor. In the Cabot plant, each unit has its own oil heaters, which are stoves fuelled with natural gas (DCMR, Permit BES98395719, 2012).

The secondary feedstock (fuel) reacts with air in the combustion chamber. This fuel can be hydrogen, carbon monoxide, methane, acetylene, alcohols or kerosene, however hydrocarbons are preferred. The hydrocarbon most suitable for the combustion is natural gas (predominantly methane). Refinery by-products can be used as well, e.g. ethane, propane and butane (Antonsen R. et al., 1976).

Reactor
The reactor is the core unit of the carbon black manufacturing process. The reactor can be divided into three main zones: the combustion, mixing and reaction zones. The particle size, the surface area and porosity of the carbon black product are determined by the rate of primary feedstock injection into the reaction zone. Generally, the production capacity of modern reactors varies from 2 to 5 tonnes of carbon black per hour.

The combustion zone is where the combustion of the fuel (secondary feedstock) occurs. The fuel also has an impact on the quality of the carbon black produced. The ratio between the amount of natural gas fuel and the amount of primary feedstock influences the material properties. The fuel is completely combusted with excess air, which is preheated in a heat exchanger by gas exiting the reactor, to temperatures in the range of 500—700 °C. This stream of air has two functions. Firstly, it is important to control the temperature of the reactor. Secondly, it ensures the complete combustion of the fuel. Consequently, the amount of process air entering the chamber, the temperature and fuel type determine the composition and temperature of the gas exiting the combustion zone, usually at temperatures between 1,320 and 1,650 °C (US Patent No. 3952087, 1976).

Additives such as alkali metal salt or potassium salts are used to influence the structure of carbon black. In the Cabot B.V. plant potassium acetate is injected (DCMR Milieudienst Rijnmond, 2012). The additives are introduced in the combustion chamber or with the primary feedstock.

The mixing zone is where the primary feedstock is introduced and mixed with the hot gas from the combustion chamber. The primary feedstock is pumped and injected into the reactor mixing with the turbulent hot gases. Additionally, the oxygen remaining from the combustion zone reacts with part of the primary feedstock. The combustion of part of the primary feedstock produces energy to trigger the pyrolysis process.

The reaction zone is where the decomposition of the primary feedstock takes place. The part of the primary feedstock that did not react with the oxygen starts to pyrolyze and spherical particles are formed. An important parameter during this process is the temperature of the reaction. This temperature determines the size of the carbon black particles formed. By adjusting the temperature, different grades of carbon black can be obtained, which allows for considerable flexibility. In particular, fine particles are most suitable for tyre manufacturing (European Commission, 2007). In the Cabot B.V. plant carbon black is typically formed at ca. 1,500 °C. The reaction temperature is controlled by water injection to avoid secondary, unwanted reactions which could reduce the carbon black quality. This quenching process occurs at temperatures below 900 °C. In the Cabot B.V. plant the temperature drops to 725 °C (DCMR Milieudienst Rijnmond, 2012).

An important parameter during the process is the air consumption factor. The remaining oxygen reacts with the primary feedstock and reduces the amount of carbon black produced. A second important parameter is the oil-injection rate which determines the temperature in the reaction chamber. The energy consumed is intended to vaporize the oil and raise the temperature to the established reaction temperature (Donnet, 1993).

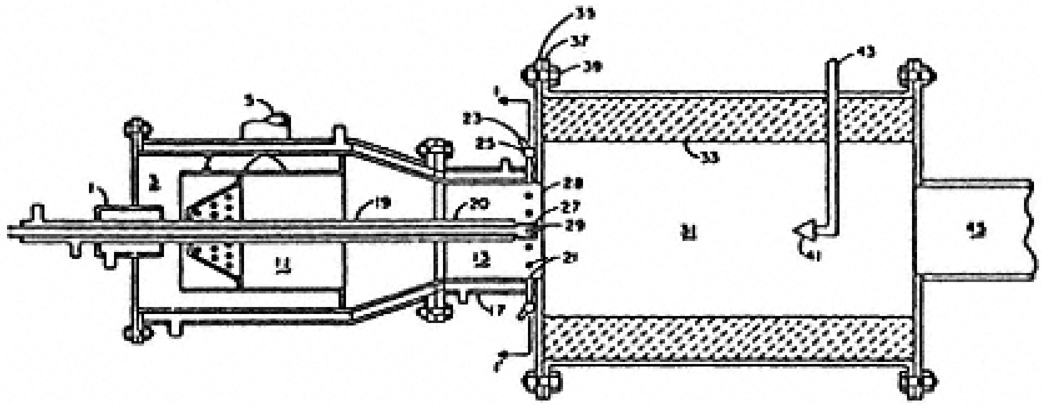


Figure 4 Cabot reactor (US Patent No. 3952087, 1976).

Separation of the carbon black product and Tail Gas.
The gas leaving the reactor which contains the desired carbon black product is called the off-gas. In order to extract the carbon black the off-gas has to be first cooled, which is usually performed by a tubular heat exchanger. The off-gas enters the heat exchanger at 700—1,000 °C and leaves at 400—600 °C. With this process the air used in the reactor is preheated. The preheated air has a temperature between 400 and 800 °C. The off-gas has to be further cooled before entering the filters as these devices operate at 230—240 °C (DCMR, Permit BES98363062, 2011). At Cabot B.V. a venturi cooler (water injection) cools the off-gas to 250 °C. This subsequent step is performed in a second heat exchanger, using the heat to preheat the primary feedstock, or for a heat boiler. In the case of a heat boiler, the steam produced can be used to preheat the primary feedstock. Once the off-gas is ready to enter the carbon black separation unit, the product is separated from the tail gas with filter bags.

The tail gas which is obtained from the separation unit can be used as a fuel due to its composition (see Table 2). Generally, 70% of the tail gas is used to produce heat, steam or electricity and the other 30% is used as a fuel in the dryers. In the latter case, the tail gas can be combusted to produce heat either directly or indirectly. The flue gases are released to the atmosphere.

At the Botlek plant, tail gas is burned in the dryers and the steam boilers. Specifically, two boilers burn tail gas to produce steam which is partly sold to the company Linde Gas (this share is assumed to be 60%) and partly used in a steam turbine to produce electricity (DCMR, 2007). Cabot B.V. is able to generate most of the electricity it needs and sells any excess electricity to the grid. The remaining steam is condensed. Cabot B.V. delivers 40 bar steam to Linde Gas Benelux B.V. and 11 bar steam to Kemira Rotterdam B.V. (DCMR, 2012).

Table 2 Ranges of tail-gas composition (European Commission, 2007; Voll & Kleinschmit, 2010)

Component	Vol.% (wet tail gas)
H_2O	29.6—50
Nitrogen (N_2)	32.7—46.2
Hydrogen (H_2)	6.6—14
Carbon monoxide (CO)	6.1—11.7
Carbon dioxide (CO_2)	1.5—5
Oxygen (O_2)	0—1.85
Methane (CH_4)	0.07—0.78
Acetylene (C_2H_2)	0.03—0.7

Final processing of the carbon black product

Carbon black is obtained from the reactors as a fluffy, low density, powdery product. Therefore, it needs to be densified. The carbon black is pelletized either via dry or wet pelletization. In this section only wet pelletization is addressed as it is used for most rubber blacks. This process consists of mixing the carbon black with water at a ratio of ca. 1 liter per kg carbon black in a pelleting machine.

Eventually, the pellets are dried in rotating dryers which are heated either externally or by hot gases circulating internally. The temperature of the carbon black leaving the dryers is between 150 and 250 °C. The heat used in the dryers can be generated by combusting the tail gas. In the Cabot B.V. plant, tail gas is burned in the combustion chambers of the tumble dryers (DCMR, 2007).

Finally, the carbon black is automatically packaged in sacks or polyethylene bags. Alternatively, the carbon black product can also be directly sent to specialized trucks for transportation.

2.2 Mass flows, energy flows and emissions

This section provides an estimate of the mass and energy balances for the production process of the Cabot B.V. plant. Furthermore, the main sources of greenhouse gas emissions in the process are identified. Finally, the production process is represented in a diagram which is divided into three main sections: *the reactor, carbon black processing,* and *steam generation (tail-gas use*).

- The reactor section includes the feedstock storage and heating, the reactor and the separation of the carbon black from the tail gas.
- The carbon black processing section includes the densification of the fluffy carbon black product, the pelletization and the dryers.
- In the steam generation (tail-gas use) section the tail gas is used to generate steam.

Mass balance
In the carbon black production process the primary feedstock (oil) and the secondary feedstock (natural gas) are used to generate thermal energy. The natural gas and part of the oil are combusted to facilitate the pyrolysis reaction and carbon black formation. In addition, part of both feedstocks ends up in the final product.

Carbon black is estimated to contain 97—99% of carbon on an elemental basis, whilst the feedstock contains approximately 90%. The yield of the carbon black production process is between 40% and 65%, depending on the desired grade of carbon black to be produced (Boultamani & Moya Rivera, 2017).

The varying process conditions make it difficult to estimate accurate material flows as well as energy flows. Another reason for uncertainty is that the quantity of feedstock converted into carbon black is unknown. An estimate of the energy efficiency and greenhouse gas emissions is provided in a report by the European Commission's Joint Research Center (Boultamani & Moya Rivera, 2017) based on Ullman's Encyclopedia of Industrial Chemistry (Voll & Kleinschmit, 2010).

The Cabot B.V. plant produces both semi-reinforcing and reinforcing carbon black products. Table 3 presents an average mass balance which corresponds to a yield of 55% (for details, see Appendix A).

Table 3 Estimated mass balance in the reactor for the production of 1 tonne of carbon black.

		Average value	Unit
INPUT	Oil	1.83	tonne
	Natural gas[6]	0.21	tonne
	Air[7]	6.15	tonne
OUTPUT	Carbon black	1	tonne
	Tail gas	10,000	Nm^3
YIELD	kg carbon black/kg oil	55	%

The amount of tail gas produced is approximately 10,000 Nm^3 per tonne of carbon black. The combustion of 1 m^3 of tail gas generates approximately 1.7 m^3 of flue gas (van Veen & Leendertse, 2002). Accordingly, the total flue gas from the tail-gas combustion is approximately 17,000 Nm^3 per tonne of carbon black.

Natural gas is also used in the boilers, the chamber burner (dryers) and the feedstock heating (DCMR, Permit BES98395719, 2012). Therefore, the emissions in the Cabot B.V. plant arise not only from tail-gas combustion but also from the additional natural gas use in these process steps.

Energy balance
Based on the available literature, the approximate energy flows per tonne of carbon black product can be calculated (see Appendix A). The results are shown in Table 4. It is assumed that part of the tail gas is used in the dryers and the rest is used to generate steam in two boilers. The steam is partly sold to other companies and the surplus of steam is used for electricity generation in a steam turbine.

6 Density of the natural gas: 0.8 t/Nm^3.
7 Density of the air: 1.2 kg/Nm^3.

Table 4 Energy flows per tonne of carbon black produced

(GJ/tonne carbon black)		
Energy consumption	Electrical	1.8
	Thermal[8]	42.1
	-of which natural gas	8.3
	-of which oil	33.8
	Total	**43.9**
Tail gas use	Dryers	5.7
	Boilers	13.3
	Total	**19.0**
Steam production	Sold to Linde Gas & Kemira	6.4
	Steam turbine	4.2
	Total	**10.6**
Electricity output	Steam turbine	1.8
	Total	**1.8**

Cabot B.V. has reported on efforts to improve the energy efficiency of the plant. In 2015, a project was developed to reduce the use of natural gas during maintenance, which reduced emissions by ca. 1 kilotonne CO_2 (Cabot , Sustainability Report, 2015). In 2016, the energy consumed by one of the tanks in which feedstocks are stored was reduced using insulating coating. There are seven tanks which are heated by steam. The coating provided a 55% reduction of the energy consumption (Cabot, Sustainability Report, 2016).

Emissions analysis
Greenhouse gas emissions occur when the fuels (natural gas and tail gas) are combusted. The emissions from carbon black production at the Cabot B.V. plant have been estimated based on assumptions on the mass and energy flows (see Appendix A). The emission factor can vary depending on the yield of the process and the quality requirements of the carbon black produced. The estimated emission factor (corresponding with 55% yield) is 3.1 tonne CO_2/tonne carbon black.

The estimate for the emission factor agrees to within 10% with the realized emission factor in 2016 (see Table 5). The difference between the estimated emission intensity and the actual emission intensity in 2016 could be due to the yield of the production process and the specifications of the carbon black produced. Rubber black (reinforcement and semi-reinforcement carbon black) has yields between 40 and 60%, while pigment blacks have lower yields which vary from 10 to 30% (van Veen & Leendertse, 2002). In the analysis of the production process, it was assumed that Cabot produces only reinforcement carbon blacks. However, in this plant also specialty blacks are produced. Additionally, a difference can be due to the additional natural gas used to support the combustion of tail gas in boilers and dryers.

8 The thermal energy refers to the energy harvested from the incomplete oil combustion and the complete natural gas combustion within the reactor.

Table 5 Emission factor for carbon black production in the Cabot B.V. plant (2016)

Parameter	Value	Unit	Source
Production capacity	80,000	tonne carbon black/year	(Port of Rotterdam, Facts and Figures, 2016)
Production volume	74,000	tonne carbon black/year	(Deloitte, 2016)
Load factor	0.93	-	Calculated
Greenhouse gas emissions	247	kilotonne CO_2-eq	(NEa, 2018)
Emission factor	3.3	tonne CO_2-eq/tonne carbon black	Calculated

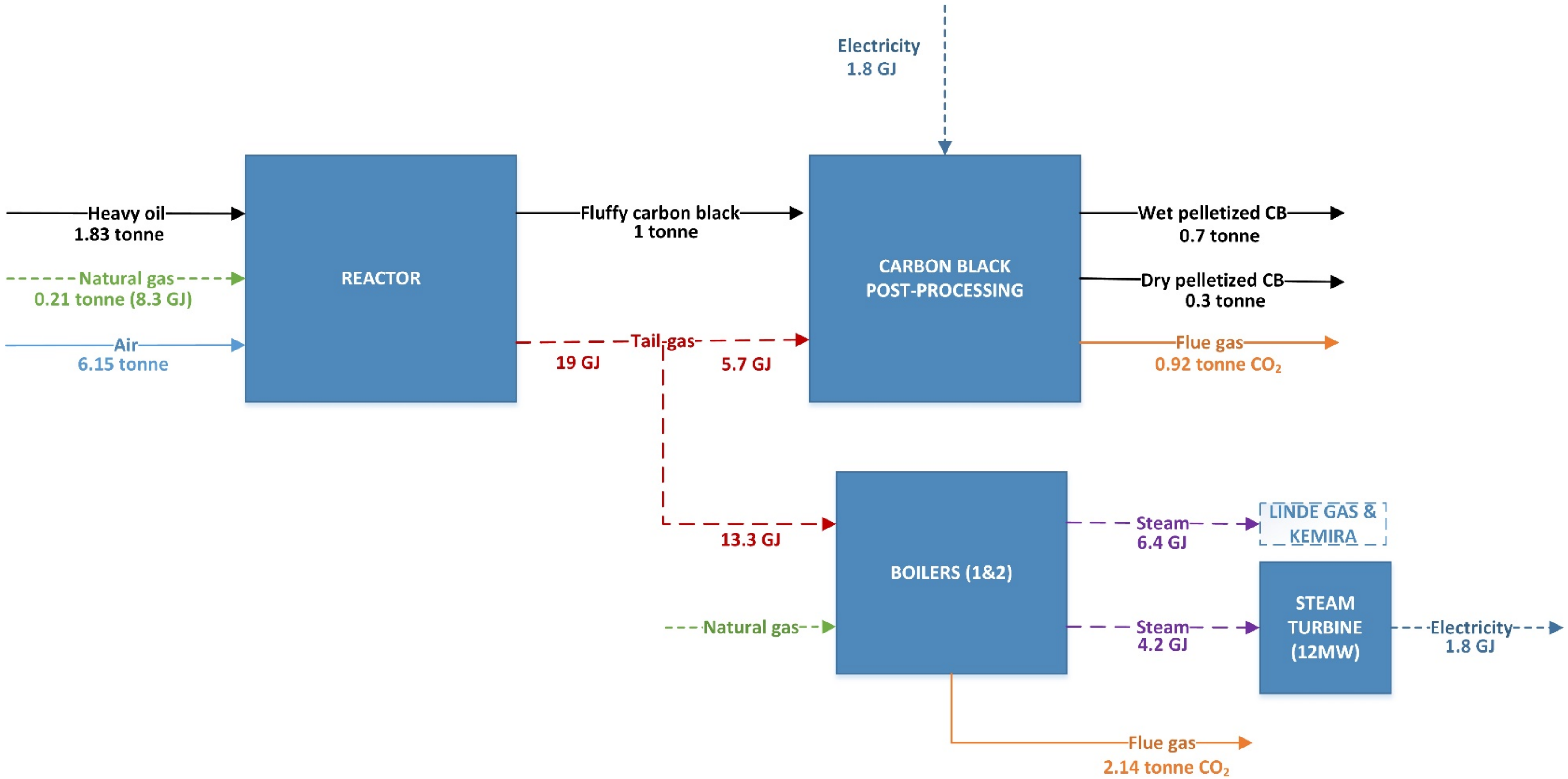


Figure 5 Estimated mass flows, energy flows and greenhouse gas emissions for the carbon black production process at Cabot B.V.

3 Carbon black products, application, and recycling

This section presents an overview of carbon black products and their applications. The types of carbon black that are produced at Cabot B.V. are discussed. Finally, the process to recycle carbon black from used tyres is described as well as the possible applications of the recycled carbon black.

3.1 Carbon black

Carbon black is a product widely used in the industry to enhance the mechanical, electrical and optical properties of materials in which it is integrated as a filler. Carbon black is commonly used in various sectors, in particular in the rubber industry. Carbon black is a reinforcing component that improves the properties of tyres (European Commission, 2007). In Ullmann's Encyclopedia of Industrial Chemistry, 35 different specifications of carbon black were identified which are used as a filler in rubber. In addition, 80 grades of carbon black were identified for use in pigments and special applications (Voll & Kleinschmit, 2010).

In 2002, 65% of the carbon black produced was consumed in the tyre manufacturing industry while the remainder was used for rubber products and diverse applications such as plastics and printing inks (see Figure 6) (European Commission, 2007).

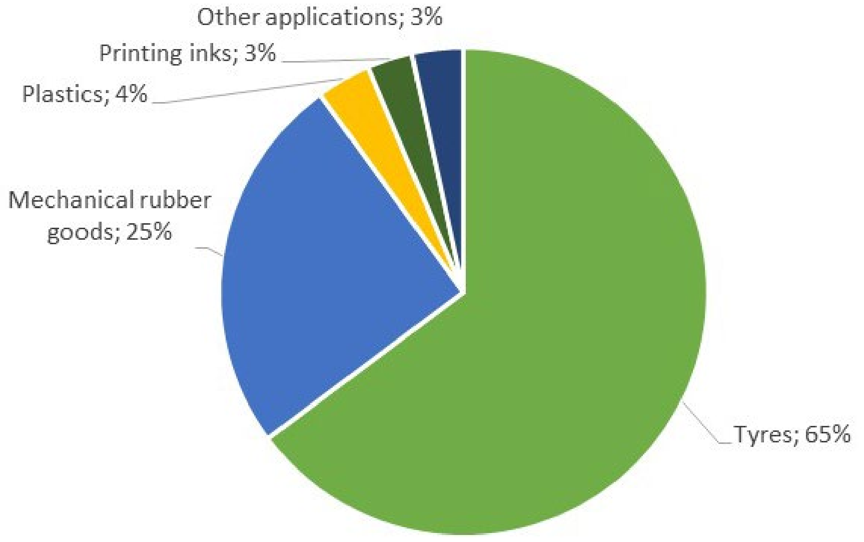


Figure 6 Applications of carbon black in 2002 (European Commission, 2007)

In 2013, the production capacity of carbon black in Europe was 1,248 kilotonnes/year. The production volume was 961 kilotonnes/year[9]. The EU Joint Research Centre (JRC) estimates that the energy consumption in the EU for carbon black production was 63.9 PJ for steam and fossil fuels (reactor) and 2.1 PJ for electricity in 2013 (Boultamani & Moya Rivera, 2017).

3.2 Products and applications

Cabot Corporation consists of four business segments: performance chemicals, reinforcement materials, specialty fluids and purification solutions. The Cabot B.V. plant produces reinforcement materials and specialty carbons and is part of the performance chemicals segment. The reinforcement materials are used for industrial rubber products. The most important customer is the tyre industry.

Cabot provides four types of reinforcement materials that enhance physical properties (such as strength, conductivity, resistivity and fluid resistance) (Cabot Corporation, 2018):

- Conductive carbon blacks modify the electrical conductivity properties of rubber according to the requirements of the final product.
- Reinforcing carbon blacks provide longer durability of rubber products, in particular tyres. They are also suitable for automotive and non-automotive parts.
- Semi-reinforcing carbon blacks are used in industrial rubber products to enhance the performance and the processing of these products.
- Ultra-clean carbon blacks can, for instance, modify mechanical properties, provide higher carbon black loading or enhance the production process for materials that require considerable electrical resistivity.

In addition, there are different specialty carbon black products integrated in fibres, semi-conductive cables, pipes, printing (toners, inks), packaging, adhesives, batteries, displays and coating (Cabot, Annual Report, 2017). These types of carbon black are used to improve conductivity, mechanical properties and static charge control, as well as to deliver UV protection. Moreover, they can be used as pigments and provide rheology control. These different grades of carbon make specialty carbon blacks suitable for a wide range of applications, for instance in the construction sector, the automotive industry, energy and inkjet printing.

3.3 Carbon black recycling

In the Netherlands, the association '*Vereniging Band en Milieu*' is in charge of the end-of-life tyres management according with the Dutch legislation for waste management. To this end the company RecyBEM provides the infrastructure and organization for collecting used car tyres (RecyBEM, 2018). There are different ways in which a tyre can be recycled, which produce recycled carbon black or recycled rubber. This section is focused on tyre recycling to obtain carbon black.

Carbon black can be recovered from tyre waste through a pyrolysis process which triggers a thermal decomposition that breaks chemical bonds. The pyrolysis of solid materials results in volatile gases with a high energy density and a carbonaceous solid (char). In the case of waste tyre pyrolysis a ~60 wt.% volatile fraction and a ~40 wt.% solid fraction are obtained (Martinez, et al., 2013) (see Figure 7).

9 Assuming a load factor of 0.77.

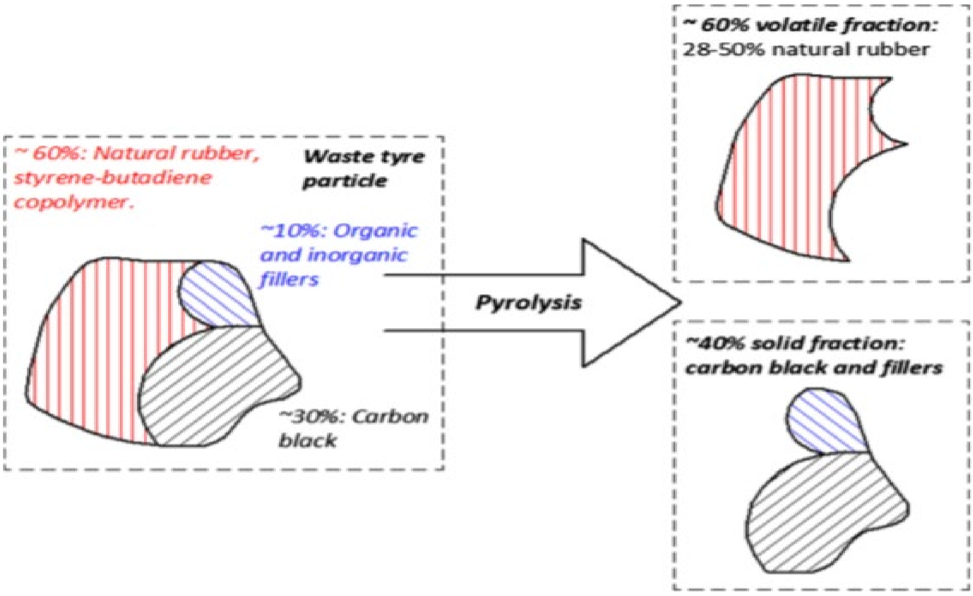


Figure 7 Tyre pyrolysis products (Martinez, et al., 2013)

The char produced mainly consists of carbon black and the volatiles have up to 50% of renewable content due to natural rubber. These volatiles are burned to produce the heat and electricity required for the pyrolysis process. The emission factor of the volatile fraction is approximately 137 g CO_2/kWh (Martinez, et al., 2013).

The company Black Bear transforms used tyres into carbon black in a plant located in Nederweert. After six years of testing and two years of production experience, Black Bear is planning to start producing on large commercial scale. To this end, Black Bear is building a new factory in the Port of Rotterdam (Port of Rotterdam, 2019). Their process is based on the pyrolysis of end-of-life tyres. The resulting products from the pyrolysis are volatile gases (10–15%), oil (45%) and carbon black (40%). The volatile gases and oil can be used to produce energy. According to Black Bear, for every tonne of carbon black produced ca. 0.5 tonne of volatile gases and ca. 1 tonne of oil are obtained (Black Bear, 2017; Black Bear, 2019).

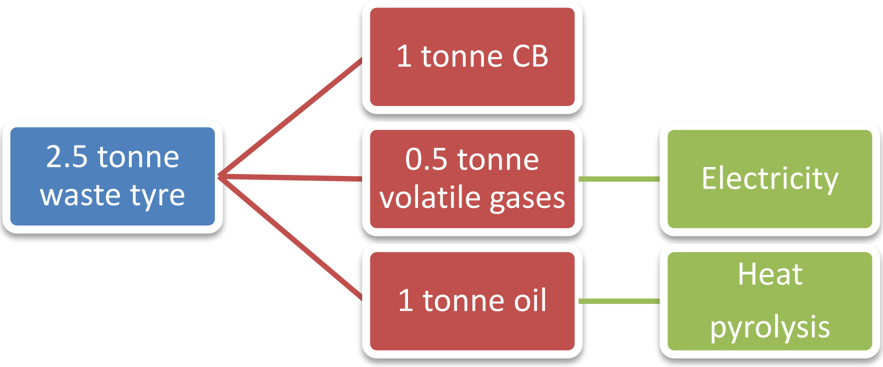


Figure 8 Diagram of the products from tyre pyrolysis in Black Bear (Black Bear, 2019)

The production process at Black Bear can be divided into five steps (Black Bear, 2019):

1) The steel contained in the tyres is removed and recycled.

2) In the Black Bear facility, the tyres are pyrolyzed in a process in which the rubber is heated in absence of oxygen. Then the rubber is decomposed into smaller molecules. The products are gas and carbonaceous char. This char contains the carbon black that was used to reinforce the tyres.
3) A de-agglomeration process breaks the char residue into smaller particles or aggregates. During this process the size of the particles is controlled in order to obtain the final product desired.
4) A pelletising process is needed to handle and store the carbon black. During this process the fluffy carbon black is densified. The procedure is similar to the one used during carbon black manufacturing, in which carbon black is combined with water in a pelletiser mixer.
5) A drying process in which the water is evaporated.

This process can close the lifecycle of a tyre in case the quality of the recycled carbon black is suitable for tyre production. According to Black Bear the resulting carbon black is used in tyres, coatings, technical rubber, plastics and inks (Black Bear, 2019).

4 Options for decarbonisation

This section describes possible decarbonisation options for the carbon black manufacturing process.

The main decarbonisation options that have been identified are:

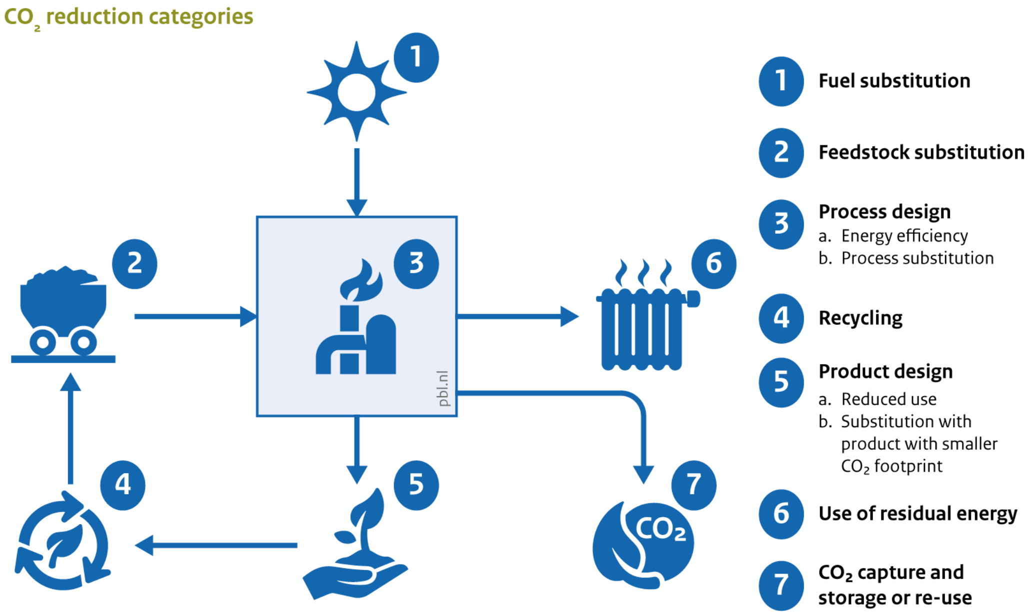
- Electrification of the process using plasma technology (for the reactor) and electric boilers (for heat production);
- Carbon Capture and Storage to reduce greenhouse gas emissions from combustion of the tail gas, and
- Substitution of the current secondary feedstock (natural gas) by bio-SNG (Substitute Natural Gas).

Other decarbonisation options that are discussed in this report are:

- Substitution of the current primary feedstock by pyrolysis oil (biomass).
- Substitution of the current primary feedstock by bio-SNG.
- Substitution of the current process (furnace black) by production of recycled carbon black from pyrolysis of tyres.

Options for efficiency improvements are not discussed. Ecofys estimates that the potential for energy efficiency improvements in the chemical industry is between 0.5% and 1.0% per year (Stork, de Beer, Lintmeijer, & den Ouden, 2018).

Section 3.3 describes the production process to obtain carbon black from pyrolysis of tyres. This process can considerably reduce the emissions in comparison with the traditional process to produce carbon black (furnace black).



Bron: PBL

Figure 9 CO_2 reduction categories

4.1 Electrification

Electrification of the processes can reduce the greenhouse gas emissions of the plant. First, electrification of the core process (the reactor) with plasma technology is discussed. Subsequently, costs for electrification of the carbon black post-processing are provided.

Review of plasma technology

New technologies based on plasma have been developed for carbon black production by the decomposition of hydrocarbons (commonly methane). These technologies also produce hydrogen. Hydrogen production is discussed in detail in MIDDEN-report 'Decarbonisation options for the production of industrial gases in The Netherlands' by Cioli et al. (in preparation).

Currently, hydrogen is usually produced by steam reforming, which causes CO_2 emissions of on average 12 kg CO_2-eq/kg H_2. Furthermore, the furnace black process is associated with an average emission of 4 kg CO_2-eq/tonne carbon black (Gautier, Rohani, & Fulcheri, 2017). With a plasma process carbon black and hydrogen can be manufactured with lower greenhouse gas emissions.

A thermal plasma is a manageable heating source (based on electricity) that can achieve high temperatures which trigger the thermal decomposition of methane. More details of the production process can be found in Gautier et al. (2017):

$$CH_4 \rightarrow C + 2H_2 \qquad \Delta H_{formation} = 75.6 \text{ kJ/mol}$$

Here, we present examples of processes based on plasma. The first process was patented by Kvaerner Engineering in Norway and transforms hydrocarbon feedstocks into hydrogen and carbon black. The hydrocarbon is pyrolyzed with energy from a plasma torch. The plasma gas used is hydrogen, which is recycled from the process itself. Therefore, the main inputs to the process are the feedstock and electricity. In this process no CO_2 is released. Another advantage of this process is that different feedstocks can be used (ranging from light gases to heavy oils). The process yields can reach almost 100% efficiency and the specific electricity consumption in this process is approximately 1.1 kWh/Nm^3 H_2 (Gaudernack & Lynum, 1998). Table 6 shows the consumption of natural gas and electricity to produce hydrogen and carbon black in a pilot plant. In this case the natural gas contains 90% of methane.

Table 6 Energy consumption and products of a pilot plasma pyrolysis plant (Labanca, 2006)

Technical Parameters	Value	Unit
Electrical energy	467	MWh/year
Natural gas	184,000	Nm^3/year
Hydrogen capacity	4.17	kg/hour
Carbon black capacity	12.5	kg/hour
Lifetime	15	years

The second process was patented by Ecole de Mine de Paris (in partnership with CNRS and TIMCAL) in France. This process uses a 3-phase AC plasma power source (Boultamani & Moya Rivera, 2017). Similarly, this process has no CO_2 emissions and almost 100% carbon yields (Fulcheri, et al., 2001).

Gasplas AS has designed another plasma reactor at small scale which has higher efficiencies and higher quality output than the Kvaerner reactor. This reactor is based on microwave plasma technology (Gasplas, 2011). The capacity reported is 200 kg H_2/day and 600 kg carbon black/day (Boultamani & Moya Rivera, 2017).

A new non-thermal plasma process has been developed at Ecole de Mines de Paris in France. This process is based on low current-high voltage discharges (Moreno-Couranjou, Monthioux, Gonzalez-Aguilar, & Fulcheri, 2009).

Large-scale plasma technology

The Kvaerner process was the first process that was scaled up. In 1997 the first industrial plant in Canada was built (Karbomont) with a capacity of 20 kilotonnes carbon black per year and 70 million Nm^3 of hydrogen. The production was stopped in 2003 due to problems with the carbon black quality control (Gautier, Rohani, & Fulcheri, 2017).

A pilot project called Seaport Pilot Plant was operated for four years until it was decommissioned in 2018. During this project Monolith developed an innovative process to produce carbon black and hydrogen from natural gas. In order to develop this process Monolith has partnered with MINES Paris Tech and Aker Solutions. This pilot project was designed to produce 90 kg carbon black/h and 350 Nm^3 H_2/h. The total capacity was 190 tonnes/year (ESA, 2013). This innovative technology is suitable for carbon black plants which have a hydrogen market (Boultamani & Moya Rivera, 2017).

Post-processing of carbon black

The carbon black manufactured in the plasma reactor is further processed in order to deliver the final product (pelletized carbon black). During this process heat is required for the dryer. For a complete electrification of the plant it is assumed that the drying process uses steam from an electric boiler.

The energy required to dry the carbon black is 2.8 GJ/tonne carbon black (see Appendix A). Accordingly, the boiler capacity required is approximately 7 MW. The total investment costs are EUR 420 thousand and the total operating and maintenance costs (O&M) are EUR 28 thousand (see Table 7).

Table 7 Technical parameters and costs of an electric boiler (Hers, Afman, Cherif, & Rooijers, 2015)

Electric boiler	Value	Unit
Technical data		
Efficiency	99	%
Technical lifetime	20	Years
Financial data		
Investment costs (equipment)	60	€/kW_e
Fixed O&M	1.1	€/kW/y
Variable O&M	0.5	€/MWh
Grid connection	130	€/kW_e

4.2 Carbon Capture, Utilisation and Storage

Carbon Capture, Utilisation and Storage (CCUS) is a solution to reduce greenhouse gas emissions from the tail gas. Scaled-up CCUS technology is already applied in the industrial sector (IEA, 2019). The potential for carbon capture in the Dutch chemical industry is estimated to be 14 megatonne CO_2 per year (Stork, de Beer, Lintmeijer, & den Ouden, 2018). This technology is based on the capture of CO_2 from the gases produced in the industrial processes.

There are three technological approaches to capturing CO_2:

1) *Post-Combustion Capture:* CO_2 is collected from combustion of fuels. In industrial processes the CO_2 is captured from the exhaust gases.
2) *Pre-Combustion Capture:* This approach is based on the gasification of carbon-containing fossil fuels or biomass producing syngas. Here the CO_2 is available at high concentration. Syngas is produced in steam methane reforming and autothermal reforming processes, and in these cases hydrogen can be produced using pre-combustion CCUS (Stork, de Beer, Lintmeijer, & den Ouden, 2018).
3) *Oxy-Fuel Combustion*: fossil fuel is combusted with pure oxygen without the presence of nitrogen. The CO_2 is separated from water vapour.

The emissions from the carbon black process come from the combustion of oil and natural gas used in the reactor. This process results in a tail gas which is combusted for heat, steam and electricity generation. The composition of this gas differs depending on the grade of carbon black manufactured. Commonly the emissions include particulate matter, CO, organics, NO_x and sulphur compounds. This exhaust gas would be similar to flue gases from coal-fired power plants having comparable levels of impurities (Last & Schmick, 2011).

The flue gas from coal-fired power plants are characterized by 13 - 15% of CO_2 (% mol) (Husebye, Brunsvold, Roussanaly, & Zhang, 2012). In the case of carbon black manufacturing it was estimated that the CO_2 concentration is around 10%[10] by volume for

[10] In the Cabot B.V. plant the total volume of flue gases produced per tonne of CB is ca. 17,000 Nm^3. Taking into account that the emission intensity in 2016 was 3.3 tonnes CO_2/ tonne carbon black and considering a CO_2 density of 1.84 kg/Nm^3 it can be roughly estimated that the concentration of CO_2 in the flue gas is 10 % by volume.

reinforcement carbon black manufacturing. Post-combustion technologies such as a membrane system or a MonoEthanol Amine (MEA) capture unit could be installed. Here, the costs for application of a MEA unit at the Cabot B.V. plant are estimated.

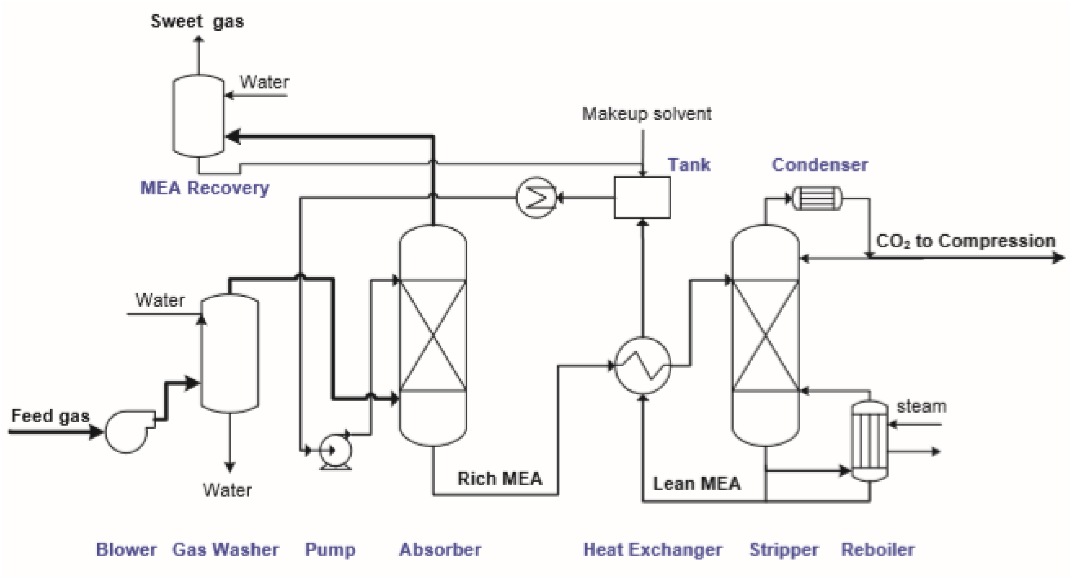


Figure 10 Post-combustion carbon capture adsorption process (Husebye, Brunsvold, Roussanaly, & Zhang, 2012)

The exhaust gas is first pressurized before entering the system. Then it is water washed and treated to remove contaminants. Subsequently, the clean gas is conveyed to the MEA solvent which purifies the gas. The rich solvent is then regenerated in the stripper with heat releasing the CO_2 at the top of the stripper.

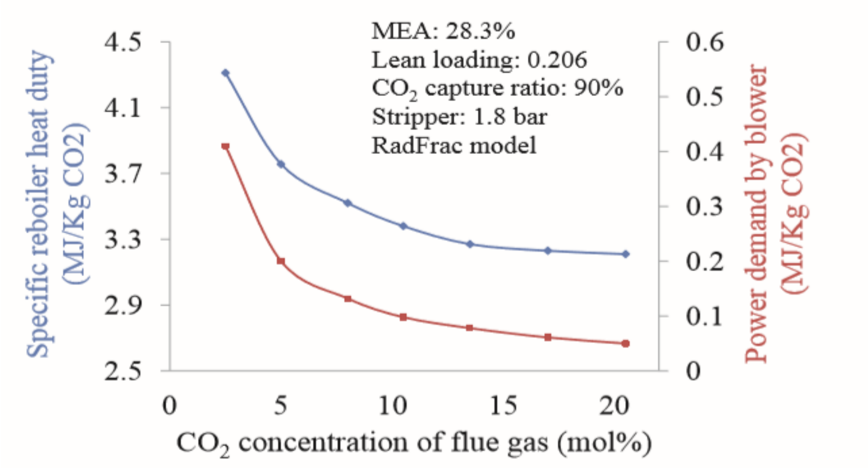


Figure 11 Energy consumption in the blower and reboiler (Husebye, Brunsvold, Roussanaly, & Zhang, 2012)

The energy consumption in the carbon capture unit occurs in the reboiler and the blower. The heat consumed in the reboiler is approximately 11.5 GJ/tonne carbon black and the power consumed in the blower is approximately 0.3 GJ/tonne carbon black. The energy consumption in the carbon capture unit has been estimated from Figure 11 considering an emission factor of 3.3 tonne CO_2/tonne carbon black and a CO_2 concentration of 10%.

The energy consumption and the costs of this process depend on the concentration of CO_2 in the stream (see Figure 11 and Figure 12). The costs were estimated from the model for a CO_2 capture capacity of 2 megatonne CO_2/year presented by Husebye et al. (Husebye, Brunsvold, Roussanaly, & Zhang, 2012). These costs are scaled to the required capacity[11] of the Cabot plant (ca. 270 kilotonnes CO_2/year).

The investment costs presented in this model include the equipment costs, direct costs (piping, erection, civil work, secondary equipment, concrete costs, steel cost and insulation) and indirect costs (engineering, administration, commissioning and contingencies costs). (Husebye, Brunsvold, Roussanaly, & Zhang, 2012).

The operating costs can be divided in fixed costs and variable costs. The fixed operating costs include maintenance, insurance and labour costs. The variable operating costs depend on the quantity of CO_2 captured, the consumption of energy (electricity, steam), cooling water and MEA make up. The costs for energy consumption in the case of the Cabot B.V. plant are considerably reduced as steam and electricity are generated from the tail gas.

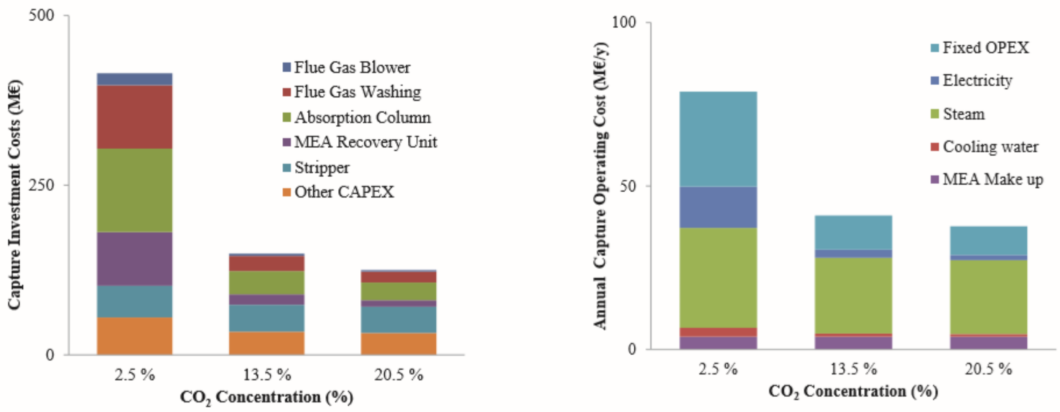


Figure 12 Investment costs and annual operating costs of capture by CO_2 concentration in the stream (Husebye, Brunsvold, Roussanaly, & Zhang, 2012)

The cost scaled for the Cabot plant are based on the results for a CO_2 concentration of 13.5% of (Husebye, Brunsvold, Roussanaly, & Zhang, 2012). In this case for a capacity of 2 megatonne CO_2-captured/y, the investment costs are EUR 125 million and the annual operating and maintenance costs are approximately EUR 16 million (excluding steam and electricity costs). These costs are scaled for the Cabot plant using a scale factor of 0.67 (Remer & Chin, 2015):

$$Cost\ 2 = \left(\frac{Size\ 2}{Size\ 1}\right)^R\ x\ Cost\ 1$$

Cost 1: known cost plant 1
Cost 2: required cost for plant 2
Size 1: capacity of the plant 1
Size 2: capacity of the plant 2
R : scale factor.

The costs are calculated for a CO_2 concentration of 13.5% and a capacity of approximately 150 kilotonne/year. The total investment costs are estimated to be EUR 32.7 million and the annual operating costs are estimated to be EUR 4.2 million/y.

11 The CO_2 capture capacity of the unit is based on an emission factor of 3.3 tonne CO_2/tonne carbon black and a plant capacity of 80,000 tonnes carbon black/year.

$$\text{Investment costs} = \left(\frac{0.27}{2}\right)^{0.67} x\ 125\ \text{mln€}/y = 32.7\ \text{mln €}$$

$$\text{Operating costs} = \left(\frac{0.27}{2}\right)^{0.67} x\ 16\ \text{mln€}/y = 4.2\ \text{mln €}/y$$

MEA technology and impurities
The efficiency of the MEA technology in the Cabot plant also depends on the impurities in the flue gas. In particular, SO_x and NO_x are reactive impurities which reduce the adsorption capacity of the solvents. These impurities react with the solvents and therefore they should be removed. The SO_2 concentration is more critical than the NO_x concentration as usually NO is the most common form of NO_x and does not react with MEA solvents (Last & Schmick, 2011).

Emissions of NO_x and SO_x from carbon black production have to be taken into account. In Europe low sulphur feedstock is used in order to limit SO_x emissions. The average content of sulphur in the feedstock is smaller than 2%. The SO_x emissions from reinforcement carbon black process are between 10 - 50 kg/tonne carbon black (European Commission, 2007).

SO_2 concentrations higher than 10 ppmv can results in process issues such as corrosion, solvent loss and foaming (Lee, Keener, & Yang, 2012). In Table 8 the concentration of SO_2 is presented. The concentration can be between 400 – 1,400 mg/Nm^3 (140 - 496 ppmv). These concentrations are presented for a sulphur content in the feedstock between 0.3 - 1.0 wt.% (European Commission, 2007).

Table 8 Concentration of emission components in the flue gas generated per tonne carbon black

Emission component	Specific emissions (kg/tonne carbon black)	Emission concentration[12] (mg/Nm^3 at 10% O_2)
Particulate Matter	0.2 - 0.4	10 - 30
Sulphur dioxide (as SO_2)	6.5 - 22.0	400 - 1400
Nitrogen oxides (as NO_2)	6.0 - 15.0	120 - 200
Volatile organic compounds	< 0.7	< 50

The sulfur concentration in this case is relatively high. Therefore, before the CO_2 separation the sulfur concentration should be reduced to a maximum of 10 ppmv. This process can be achieved through a flue gas desulfurization unit (FGD). The wet FGD is commonly used and has low operating costs. Information about desulphurization technology is described by Lisnic & Jinga (Lisnic & Jinga, 2018). Moreover, desulphurization options were proposed for the carbon black industry in the Best Available Techniques Reference (BREF) document (European Commission, 2007). Cases of desulphurization in the European carbon black industry were still not existing by 2007.

In 1999 a producer of speciality carbon black in the Netherlands stated that their emissions of NO_x were 700 - 800 mg/Nm^3. These emissions have been reduced using low NO_x burners in the tail-gas boiler. However, reducing the concentration of NO_x before entering the carbon capture unit might be required. In this document an end-of-pipe deNO_x solution is proposed,

[12] Emission concentrations at 273.15 K, 101.3 kPa under dry conditions, standardised to 10% O_2. This oxygen percentage would be representative for a situation where all off-gases are emitted through a central stack (European Commission, 2007).

however other solutions might be suitable as well (European Commission, 2007). Information about two Dutch plants was used to estimate the costs for these technologies (one of these plants is Cabot. Moreover, both plants had the same size therefore the results are considered valid for both plants).

The investments for a combined deSOx/deNO$_x$ system were estimated in 2002. The investment costs (expressed in euros of 2017) are EUR 11.4 million and the operating costs EUR 1.55 million[13]. Both carbon black companies considered the estimates for the investments too low (van Veen & Leendertse, 2002).

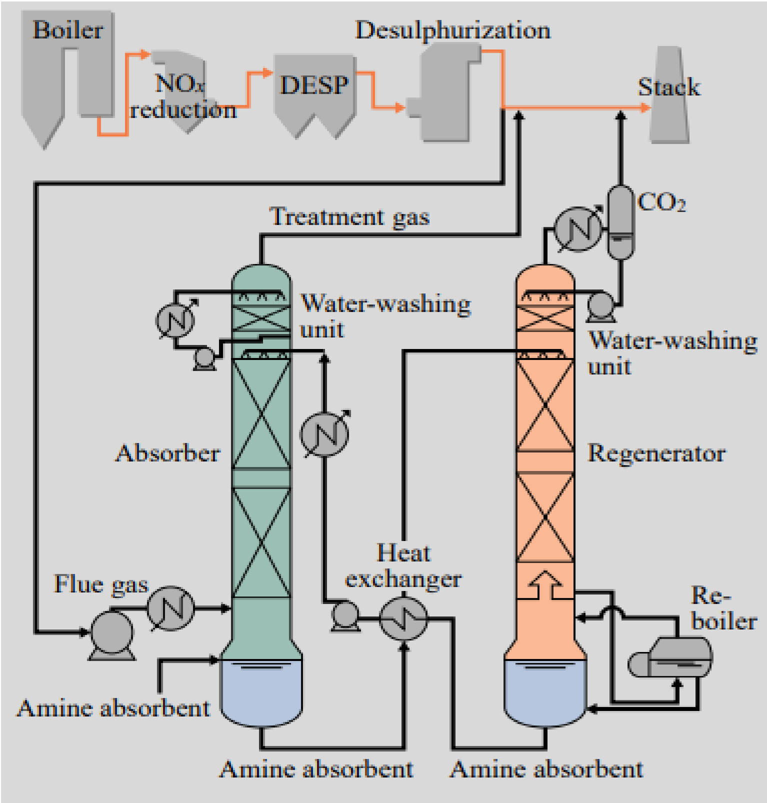


Figure 13 Process of CO_2 removal for coal power plants (Kikkawa, Ishizaka, Kai, & Nakamoto, 2008)

Transport and storage of CO_2

The feasibility of carbon capture technology depends on the infrastructure available for transport and storage of the captured CO_2. Gasunie and EBN have analysed the possibility of developing a basic CO_2 infrastructure in the Port of Rotterdam which would enable the storage of CO_2 beneath the North Sea (Port of Rotterdam, 2017). This project is called *Porthos* and was presented as technically viable for capturing, transporting and storing CO_2 (Port of Rotterdam, 2018). The goal is to store between 2 and 5 megatonnes of CO_2 in the North Sea each year by 2030 (Rotterdam, Gasunie, & EBN, 2019). Part of the CO_2 captured will also be used for greenhouse horticulture in South Holland. The costs of transport and storage will depend on the contracted services (Port of Rotterdam, Gasunie, & EBN, Customers, 2019).

In the presented costs for carbon capture, the transport and storage of CO_2 are not included. These costs are estimated to be ca. EUR 10/tonne CO_2. The costs for flue gas capture are

[13] The original investment costs from 2002 are EUR 9.94 million and the operating costs are EUR 1.35 million.

expected to drop by 25% to 30% by 2025 - 2030 due to technical improvements and innovation (Warmenhoven, Kuijper, van Soest, Croezen, & Gilden, 2018).

CO_2 storage is a temporary solution to reduce the CO_2 emissions in the Port of Rotterdam. As a long-term solution, the captured CO_2 could be used as a feedstock for other processes in the area. However, the possibility of circular alternatives to use the CO_2 captured is currently limited (Rotterdam CCUS, 2019). Alternatively, the CO_2 captured could be used to produce synthetic natural gas through the methanation of the carbon dioxide. This reaction is called the Sabatier process and is a hydrogenation reaction.

$$CO_2\,(g) + 4\,H_2\,(g) \Leftrightarrow CH_4(g) + 2H_2O\,(l)$$

The methane produced could be used as a feedstock for the carbon black process (see Section 4.3). The use of natural gas as a feedstock implicates uncertainties regarding the efficiency of the production process and the changes required to the process. Therefore, this option is not considered for a full analysis.

4.3 Substitution of natural gas by bio-SNG

The fuel or secondary feedstock commonly used in the furnace black process is natural gas, but propane, butane, synthetic gas or tail gas can also be used (Donnet, 1993). In order to reduce the emissions in the reactor bio-SNG could substitute the natural gas. Bio-SNG is obtained from biomass and it can be produced by upgrading biogas (fermentation of biomass) or synthetic gas (gasification of biomass) to the same quality as natural gas (Hanschke, Londo, & Uyterlinde, 2010).Therefore, bio-SNG can be transported in the pipeline infrastructure available for natural gas. Possibly, biogas that has not been upgraded may be used as well. This may affect the quality of the product or the conditions in the reactor.

The natural gas consumed in the reactor is 8.3 GJ/tonne carbon black. The corresponding emissions are 0.47 tonne CO_2/tonne carbon black (14% of total emissions). This decarbonisation solution would not entail changes in the current production process. The potential for the use of bio-SNG in the industry depends on the availability of biomass in the future (Honoré, 2017).

4.4 Other decarbonisation options

In this section two alternative decarbonisation options are described. These alternatives are based on the substitution of the feedstock (oil) by bio-based feedstocks (pyrolysis oil and bio-SNG).

Pyrolysis oil
An alternative decarbonisation option is the substitution of the current feedstock (ethylene cracker residue) by a pyrolysis oil. Pyrolysis oil is produced from biomass. Bio-based carbon black was made for the first time by researchers at the RISE Energy Technology Centre in Sweden. They used pyrolysis oil from renewable solid biomass in an experiment, which simulates the current production process in the industry in which the oil is sprayed in a reactor at high temperatures. The yield from this process was limited, 10.6% by weight of the fed pyrolysis oil. The researchers expect that the yield will improve when the scale is increased (BIO4ENERGY, 2018).

In the Port of Rotterdam production, storage and shipment of biofuels are possible. Raw materials and biofuels can be provided from all around the world. Moreover, in the port of Rotterdam there are five biofuel production facilities. The biofuels produced are biodiesel, bio-ethanol and renewable diesel which are produced for road transport, shipping and aviation. These facilities could provide the bio-oil required for the carbon black production process (Port of Rotterdam, 2019).

Bio-SNG

In the past natural gas was used in the furnace black process to produce carbon black (European Commission, 2007). Therefore, synthetic natural gas from biomass (bio-SNG) could be used to produce carbon black. This gas is obtained upgrading synthesis gas to natural gas. The synthesis gas is produced through gasification of biomass at high temperatures (Hanschke, Londo, & Uyterlinde, 2010).

Costs and estimations for this solution are not included due to uncertainties regarding the new requirements for this process (design of a new reactor) and changes in the production process.

The quantity of bio-SNG needed for the production process is based on an experimental study of carbon black formation from incomplete combustion of natural gas. This study is based on oil furnace processes. The gas furnace designed for the experiment can produce 5 to 10 kg carbon black per hour. The yield can reach 30%[14] (Moghiman & Bashirnezhad, 2007). However, in the large scale this can differ. Moreover, the quality of carbon black produced is not specified.

In Keipi et al. (2015) a techno-economic analysis of thermal decomposition of methane (TMD) to produce hydrogen and carbon black is presented. Part of the methane is combusted in a burner and the flue gas is used for the thermal decomposition reaction of methane. The mass balance of the process is presented in Table 9.

Table 9 Mass balance of thermal decomposition of methane (Keipi, Hankalin, Nummelin, & Raiko, 2015)

Mass balance	Value	Unit
Input		
Methane	3	kg/s
Air	8.1	kg/s
Output		
Product gas[15]	10.2	kg/s
Product carbon	0.9	kg/s

Based on an expected 30% yield, it is estimated that for a production rate of 1 tonne carbon black/h, the amount of feedstock needed is approximately 3.33 tonne bio-SNG. The production of bio-SNG is achieved through a gasification process. The gasification requires heat which is supplied by the combustion of part of the biomass (fuel) in direct gasification. Alternatively, this heat could be supplied externally in case of indirect gasification (van der Meijden, Rabou, van Boven, van der Drift, & Overwijk, 2014). In this case direct gasification is assumed. The electricity consumption for producing bio-SNG is assumed to be 2% of the thermal input (Aranda, van der Drift, & Smit, 2014). The gasification process transforms

[14] The yield is expressed in kg carbon black/kg feedstock.
[15] The product gas contains 28% of H_2 and 15.2% of methane in molar composition. In addition it contains 5.4% of CO_2. The lower heating value (LHV) of the product gas is 10.4 MJ/kg (Keipi, Hankalin, Nummelin, & Raiko, 2015).

biomass into a gas with the same quality as natural gas (bio-SNG). The energy efficiency of the gasification process to obtain synthetic gas is 65%.

The investment costs and operational costs are presented in Table 10. The investment costs include gasification, cleaning, upgrading and feeding to the gas network. In this case the gas is used in the plant as a feedstock.

Table 10 Techno-economic parameters of bio-SNG production (ECN, 2017)

Techno-economic parameters	Value	Unit
Size	2,397	Nm^3/h_{output}
Full load hours	7,500	h/a
Investment costs	3,250	€/kW_{output}
Fixed O&M	285	€/kW_{output}
Energy content	9 - 13	GJ/tonne
Raw material	50	€/tonne

5 Discussion

The feasibility of application of the decarbonisation options presented in Chapter 4 depends on the type of carbon black produced. The specification of each grade of carbon black corresponds with specific physical and chemical properties. These properties depend on the raw materials and the production process.

During the process the properties are controlled by the proportion of primary feedstock, secondary feedstock and air in the reactor. The size of the particles produced decreases with higher ratios of air due to an increase of temperature in the reaction zone. Thus, the yield depends on the type of carbon black produced and the type of feedstock used. Normally, the yields for carbon black production are between 40 and 60%. However, for high-surface-area pigment blacks, which have a smaller size than the rubber blacks, yields between 10 and 30% are common (van Veen & Leendertse, 2002).

Cabot B.V. produces two types of carbon black: reinforcement materials and specialty blacks. These have different yields whilst the number of reactors used for each product is unknown. In Section 3 the emissions are estimated assuming a 55% yield, which corresponds with reinforcement blacks production only. As a consequence, the real emissions may be higher than the estimated emissions.

The type of carbon black produced is important as there are different product markets. For example, the quality requirements for reinforcement blacks and fillers are typically less stringent than for specialty blacks. The feedstock used for specialty blacks should have low sulfur content. In 2002, it was stated that the price of specialty blacks was two times the price of rubber blacks (van Veen & Leendertse, 2002).

The most relevant decarbonisation options for the Cabot B.V. plant are the electrification with plasma technology, CCUS and the substitution of the fuel by bio-SNG. Alternative solutions are the substitution of the feedstock by bio-based fuels (e.g. pyrolysis oil, bio-SNG).

In 2002, the plasma technology for carbon black production was considered to have low perspectives because the quality of the products did not meet the specifications required (van Veen & Leendertse, 2002). However, in the US this technology has been developed further by Monolith. Hydrogen is also produced in this process and therefore the plant should preferably be located near hydrogen consumers. Cabot is located in the Port of Rotterdam where there is already an infrastructure to transport hydrogen. The implementation of this technology would require changing the reactors of the plant, but the post-processing of the carbon black would remain the same. Finally, it is important to highlight that the electrification of the process is considered a decarbonisation option provided that the electricity comes from low-carbon sources.

Carbon capture technology is a mature technology that can be used to capture the CO_2 from the flue gas. In the Cabot B.V. plant the flue gas is produced in dryers and boilers and therefore there could be more than one stream. The estimated concentration of CO_2 in the flue gas is 10%. In the future services for CO_2 transport and storage could be contracted in the Port of Rotterdam. The CO_2 captured can be delivered to greenhouses or used in the nearby industries. Moreover, the CO_2 captured could be used to produce methane in a Sabatier process. The methane produced could be used as a fuel or as a feedstock. The latter would require changes in the production process (reactor).

In the past the use of natural gas as a primary feedstock was common. However, for economic reasons the use of petrochemical oils became more suitable. Natural gas can be used as a feedstock in the furnace black process, but this would require a change to the design of the reactor and the yield would drop due to lower contents of carbon in comparison with petrochemical oils. Moreover, the conditions required to produce the different types of carbon black might be different.

Similarly, bio-SNG can be used as a primary feedstock in the furnace black process. The main barriers to the use of bio-SNG may be the new equipment required to use this feedstock, as well as economic barriers due to the competitive global market. Moreover, the applicability of bio-SNG depends on biomass availability and prices.

Alternatively, the petrochemical oils currently used in the reactor could be substituted by pyrolysis oils from biomass. However, this decarbonisation option is still in a research phase.

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Appendix A: Mass flows, energy flows and emissions

This appendix contains estimates for the mass flows, energy flows and emissions of the carbon black production process of Cabot B.V.

The mass flow for a modern high-performance reactor is presented in Table 11, based on data from Ullman's Encyclopedia of Industrial Chemistry (Voll & Kleinschmit, 2010). The mass flow depends on the grade of carbon black produced. In the case of Cabot B.V. both semi-reinforcing and reinforcing carbon black are manufactured. Therefore, a representative mass flow for the Cabot B.V. is based on an average. The average rates for inputs and outputs have been calculated by the European Commission's Joint Research Centre (Boultamani & Moya Rivera, 2017).

Table 11 Mass flows in the furnace black process

		Semi-reinforcing carbon black	Reinforcing carbon black	Average
INPUT	Oil	2.5 – 3.3 tonne/h	1 – 1.5 tonne/h	1.83 tonne /tonne carbon black
	Natural Gas	300 - 550 m^3/h	280 - 440 m^3/h	0.21 tonne/ tonne carbon black
	Air	7,000 - 10,000 m^3/h	6,000 - 7,000 m^3/h	6.15 tonne/ tonne carbon black
OUTPUT	Carbon black	1.5 - 2 tonne/h	1 - 1.5 tonne/h	1 tonne
Yield[16]		50 - 60%	40 - 60 %	55%

Using these mass flows, the emission factor for carbon black production is calculated based on the carbon content of the input flows and the products. This calculation is described in guidelines for the calculation of emissions from production processes of petrochemicals, including carbon black (see Section 3.9 of the 2006 IPCC guidelines (IPCC, 2006)).

The primary fossil fuels are intended to be used as raw material. However, in this process part of the primary feedstock is combusted to produce heat. The tail gas is a secondary product that is combusted to produce steam, power and heat for the dryers. The amount of tail gas produced per tonne of carbon black is approximately 10,000 Nm^3. The combustion of 1 m^3 of tail gas generates approximately 1.7 m^3 of flue gas (van Veen & Leendertse, 2002). Accordingly, the total amount of flue gas produced in the furnace black process is

16 The yield is expressed in kg carbon black/kg oil.

approximately 17,000 Nm^3 per tonne of carbon black. This is an approximation that does not consider the additional natural gas added to support the combustion of the tail gas which has a low calorific value due to its moisture content (van Veen & Leendertse, 2002).

The Tier 2 methodology to calculate the CO_2 emissions is based on a mass balance approach. The primary and secondary feedstocks as well as the products have to be defined. In the Cabot B.V. plant the inputs are natural gas and oil. The outputs are carbon black and tail gas. However, the tail gas is burned in the plant and therefore it is accounted for in the total emissions reported in the ETS. In the following, it is assumed that the carbon in the tail gas is part of the CO_2-emissions.

The equation used for the balance is:

$$ECO2_{CB} = \{\sum_{k}(FA_{CB,k} \times FC_k) - [\mathrm{PP}_{CB} \times \mathrm{PC}_{CB}]\} \times 44/12$$

$ECO2_{CB}$ = CO_2 emissions from production of carbon black, tonne CO_2/tonne carbon black
$FA_{CB,k}$ = consumption of feedstock k for production of carbon black, tonnes k/tonne carbon black
FC_k = carbon content of feedstock k, tonne carbon/tonne k
PP_{CB} = production of carbon black, tonne
PC_{CB} = carbon content of carbon black, tonne carbon/tonne carbon black

The carbon content and the calorific value of the inputs and the output are listed in Table 12. The specific carbon content of the carbon black and the oil are retrieved from the IPCC guidelines (IPCC, 2006). The calorific values for the fuels haven been collected from the Netherlands list of energy carriers and standard CO_2 emission factors (Zijlema, 2018). The calorific value of carbon black has been obtained from a permit (DCMR, 2012) and the Best Available Techniques Reference Document (European Commission, 2007).

Table 12 Characteristics of the inputs and outputs of the furnace black process

	Specific carbon content (tonne carbon/ tonne X)	Calorific value
Carbon black (CB)	0.97	33 MJ/kg
Primary feedstock (oil)	0.90	41 MJ/kg
Fuel (natural gas (NG))	0.75	31.65 MJ/Nm^3

These values can be used to obtain the emission intensity of the carbon black production process. The emission intensity is calculated by diving the total emissions by the amount of carbon black produced:

$$\mathrm{EF}_{CB} = \{(0.21 \text{ tonne N} \times 0.75 \text{ tonne C/tonne N} + 1.83 \text{ tonne oil} \times 0.90 \text{ tonne C/tonne oil} - (1 \text{ tonne CB} \times 0.97 \text{ tonne C/tonne CB}\} \times 44/12 = 3.1 \text{ tonne } CO_2\text{/tonne CB}$$

Subsequently, the energy balance of the process can be derived. The natural gas is completely combusted in the reactor while the feedstock is partly combusted. Therefore, the thermal energy is generated from both inputs. The fuel is completely combusted with excess air, the remaining air is consumed in the combustion of the feedstock. Based on the yield, 45% of the oil is combusted to provide the energy needed.

The thermal energy released from the fuel can be calculated using the calorific value of natural gas (see Table 12):

$$E_{fuel} = 31.65\ \mathrm{MJ/Nm_3\ N} \quad \times (0.21\ \mathrm{tonne\ N} \quad /\mathrm{tonne\ CB})/\ (0.8\ \mathrm{kg\ N} \quad /\mathrm{Nm_3\ N} \quad) = 8.3\ \mathrm{J} \quad /\mathrm{tonne\ CB}.$$

The thermal energy from the oil combustion is calculated using the calorific value of oil (see Table 12) and the assumption that 45% of the oil is combusted:

$$E_{feedstock} = 41\ \mathrm{MJ/kg\ \ oil} \times (1.83\ \mathrm{tonne\ oil/tonne\ CB}) \times 45\% = 33.8\ \mathrm{J} \quad /\mathrm{tonne\ CB}.$$

The thermal energy produced in the reactor is 42 GJ/tonne carbon black. Moreover, in the process the tail gas is used to produce electricity, steam and heat. The volume of the tail gas is assumed to be 10,000 Nm^3/tonne carbon black. The lower heating values of the tail gas is between 1,700 and 2,100 kJ/m^3 (Voll & Kleinschmit, 2010). The total thermal energy from the tail gas is approximately 19 GJ/tonne carbon black.

$$E_{tail\ gas} = 1.9\ \mathrm{MJ/Nm_3\ tail\ gas} \times (10{,}000\ \mathrm{Nm_3\ tail\ gas/tonne\ CB}) = 19\ \mathrm{J} \quad /\mathrm{tonne\ CB}$$

As the tail gas has a low calorific value additional natural gas is added to the tail gas. This amount of natural gas is not taken into consideration.

Natural gas is also used to heat the oil before it enters the reactor. The CO_2-emissions that result should be taken into account in the carbon footprint of the carbon black production. Therefore, an estimate is made of the amount of natural gas which is used to heat the oil, assuming that the temperature of the oil needs to increase from 95 ^oC (average temperature in the tanks) to 200 ^oC (average temperature of the oil before entering the reactor). The specific heat is an average of the minimum and the maximum value for fuel oil (ToolBox, 2018).

$$\mathrm{H} = \Delta\mathrm{T} * \mathrm{cp} * \mathrm{m}$$

$$\mathrm{H} = (200 - 95)\ \mathrm{K} \times (1.88\ \mathrm{KJ/kg\ K}) * 1{,}830\ \mathrm{kg/tonne\ CB} = 0.36\ \mathrm{J} \quad /\mathrm{tonne\ CB}$$

From this result, it is concluded that the emission due to the preheating of the oil can be neglected.

It is estimated that in the dryer, 1 tonne H_2O/tonne carbon black is heated from 18° C to 250° C (Donnet, 1993). The energy required is calculated using the specific enthalpy for saturated steam at 250° C (TLV, 2019) and is approximately 2.8 GJ/tonne carbon black.

$$E_{drying} = (2{,}801\ \mathrm{KJ/kg}\ H_2\mathrm{O}) * \mathrm{tonne}\ H_2\mathrm{O/tonne\ CB} = 2.8\ \mathrm{J} \quad /\mathrm{tonne\ CB}$$

Table 13 shown the estimated energy required to produce 1 tonne of carbon black.

Table 13 Energy required to produce 1 tonne carbon black

	Energy consumption (GJ/tonne CB)
Electrical[17]	1.8
Thermal[18]	42.1
of which natural gas	8.3
of which oil	33.8
Total	**43.9**

[17] The electricity consumption for a plant with a production around 75,000 is approximately 1.8 GJ/tonne carbon black (Boultamani & Moya Rivera, 2017) (European Commission, 2007).

[18] The thermal energy refers to the energy harvested from the incomplete oil combustion and the complete natural gas combustion within the reactor.

The tail gas is used to produce heat, steam and power. From the literature is it estimated that 30% of the tail gas is used in the dryers and 70% for steam and power generation. In the Cabot B.V. plant, two boilers and a 12 MW steam turbine are installed. According to the description in the environmental permits, the tail gas is combusted in boilers to produce steam (see Section 2.1). The efficiency of the waste gas boilers is assumed to be 80% *(EPA, 2015)*.

Table 14 Tail-gas use in the Cabot B.V. plant

	Tail gas use (GJ/tonnes CB)
Dryers	5.7
Boilers	13.3
Total	**19.0**

It is assumed that part of this steam (60%) is sold to other industries and the rest (40%) is used to produce electricity in a steam turbine with an assumed efficiency of 42%. Condensing steam turbines can reach efficiencies of 40 - 45 % *(Goovaerts, Luyckx, Vercaemst, De Meyer, & Dijkmans, 2002).*

Table 15 Distribution of the steam from the tail gas produced at the Cabot plant

	Steam production (GJ/tonne CB)	Electricity output (GJ/tonne CB)
Sold to Linde Gas & Kemira	6.4	-
Steam turbine	4.2	1.8
Total	**10.6**	**1.8**

The tail-gas exiting the reaction is distributed as shown in Table 16. There are four main emission points where gases are released: the venting of non-combusted tail gas, the gases released from tail-gas combustion in boilers and dryers, and gases released in the filter systems.

Table 16 Distribution of the tail gas exiting the reactor in the production process per tonne(carbon black)

Section	Tail gas (Nm^3/tonne carbon black)	Flue gas (Nm^3/tonne carbon black)	CO_2 emissions (tonne/tonne carbon black)
Carbon black processing (dryers)	3,000	5,100	0.9
Boilers (1&2)	7,000	11,900	2.2
Total	**10,000**	**17,000**	**3.1**

Finally, Table 17 compares the estimate for the emission factor (3.1 tonne CO_2-eq/ tonne carbon black) agrees to within 10% with the realized emission factor for 2016 (3.3 tonne CO_2-eq/ tonne carbon black).

Table 17 Emission factor for carbon black production in the Cabot B.V. plant for 2016

Parameter	Value	Unit	Source
Production capacity	80,000	tonne carbon black/year	(Port of Rotterdam, Facts and Figures, 2016)
Production volume	74,000	tonne carbon black/year	(Deloitte, 2016)
Load factor	0.93	-	Calculated
Greenhouse gas emissions	247	kilotonne CO_2-eq	(NEa, 2018)
Emission factor	3.3	tonne CO_2-eq/ tonne carbon black	Calculated